

**IN THE UNITED STATES PATENT  
AND TRADEMARK OFFICE**

Applicant(s): Yasuyuki Mizuno et al  
Serial No.: 10/529,738  
Filed: March 30, 2005  
For: RESIN COMPOSITION FOR PRINTED WIRING BOARD AND  
VARNISH, PREPREG AND METAL CLAD LAMINATED BOARD  
USING THE SAME  
Art Unit: 1796  
Examiner: Robert E. Sellers

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

**DECLARATION UNDER 37 CFR 1.132**

SIR:

I. I, Yasuyuki Mizuno, a first inventor of this case,  
declare and say as follows.

I got a Bachelor degree in engineering from Shinshu University in 1991, and entered Hitachi Chemical Company, Limited in April 1991. I have made researches in resin materials and substrates for printed wiring boards in Hitachi Chemical Company, Limited since September 1993. I studied the Official Action dated January 16, 2009 received in the parent application of said application.

In order to show that the present invention has the effects in the claimed range of biphenyl structure-containing epoxy resin in direct comparison of the example disclosed in the closed prior art (Mizuno et al.), I have conducted 2nd additional experiments as mentioned below under my

supervision.

## II. Additional experiments

The additional experiments show the unexpectedly better results achieved by the presently claimed invention in effects in direct comparison of presently claimed biphenyl epoxy resin composition with the brominated bisphenol A epoxy resin ESB-400T formulation disclosed in the closest prior art (Mizuno et al.).

In other words, the formulation of example 19 of Mizuno et al. with the brominated bisphenol A epoxy resin ESB-400T are compared with the formulation where that brominated bisphenol A epoxy resin is replaced with the present biphenyl epoxy resin.

## EXPERIMENT

### (1) Sample

Resin varnishes (EX-15 to 20) are prepared according to the formulation amount as shown in Table 2. The numberings of experiments are in consecutive order to the experiments in the declaration filed in June 16, 2009.

This EX-15 is a replicated composition based on the description of example 19 of the prior patent (Mizuno et al), EX-16 uses equivalent weight amount of biphenyl type epoxy resin (YX-4000) in place of the brominated bisphenol A epoxy resin (ESB-400T) for example 19 of Mizuno et al, and EX-17 uses equivalent epoxy equivalence ratio of biphenyl type epoxy resin (YX-4000) in place of brominated bisphenol A epoxy resin (ESB-400T) for example 19 of Mizuno et al. As the epoxy equivalence ratio of brominated bisphenol A epoxy resin (ESB-400T) (EEW:400) doubles that of biphenyl type epoxy resin (YX-4000) (EEW:190), thus, two comparisons are made in the equivalent weight amount and equivalent epoxy equivalence ratio.

On the other hand, EX-18 is a replicated composition with equivalent formulation of example 16 of the present application, EX-19 uses a varnish composition where the brominated bisphenol A epoxy resin (ESB-400T) is removed from the formulation of example 16 of the present application making it solely of the biphenyl type epoxy resin (YX-4000) systems, and EX-20 is a varnish composition where biphenyl type epoxy resin (YX-4000) is removed from the formulation of EX-18 making it solely of the brominated bisphenol A epoxy resin (ESB-400T) systems.

(a) Varnish

(Preparation of varnish)

EX-15

A 2-liter four-necked separable flask equipped with a thermometer, cooling tube and stirring device was charged with toluene, 2,2-bis(4-cyanatophenyl)propane and p-(a-cumyl)-phenol (available from Tokyo Kasei Kogyo Co., Ltd.). The mixture was then incorporated with zinc naphthenate as a reaction promoter, after it was kept at 120°C as liquid temperature, and heated for 4 hours (reactant concentration: 75% by weight) to synthesize the phenol-modified cyanate oligomer, where the reaction process was controlled to have a cyanate compound monomer conversion of about 55%. This conversion was confirmed by liquid chromatography (Chromatograph: pump; manufactured by Hitachi, Ltd; L-6200, RI detector; L-3300, and columns, Manufactured by TOSOH CORPORATION, TSKgel-G4000H and G2000H, solvent: tetrahydrofuran, concentration: 1%). The same chromatograph was used to determine number-average molecular weight of the product with a calibration curve of the standard polystyrene. The phenol-modified cyanate ester oligomer had a number-average molecular weight (Mn) of 1,430 on the cyanate monomer-free basis. It was also confirmed by the same chromatograph that the elution peak of p-(a-cumyl)phenol disappeared.

The phenol-modified cyanate oligomer was cooled to room temperature, and incorporated with brominated bisphenol A type epoxy resin (manufactured by Sumitomo Chemical Company, Ltd; ESB400T, available from Sumitomo Chemical Co., Ltd.), methylethylketone and the same zinc naphthenate. The mixture was stirred for 1 hour, to prepare the varnish containing non-volatile content at 65% by weight and a gelation time (at 160°C) of around 300 seconds. In table 2, the amounts of each material formulated in the varnish are shown.

#### EX-16

A resin varnish having a non-volatile concentration of about 65 % by weight was prepared in analogous to the procedure and formulation of EX-15 except that a biphenyl type epoxy resin (YX-4000, available from Japan Epoxy Resin Co.) is used instead of brominated bisphenol A type epoxy resin (ESB400T).

#### EX-17

A resin varnish having a non-volatile concentration of about 65 % by weight was prepared in analogous to the procedure and formulation of EX-15 except that the formulation was changed to the amount shown in Table 2 in the above EX-15 formulation and that biphenyl type epoxy resin (YX-4000) is used instead of brominated bisphenol A type epoxy resin (ESB400T).

#### EX-18

In a 3-liter four-necked separable flask equipped with a thermometer, a cooling tube and a stirring device, toluene and polyphenylene ether resin (PKN4752, available from GE Japan Co.) were charged, and the mixture was heated to 90°C and dissolved under stirring. Next, a phenol novolac type cyanate ester resin (REX-371, available from Ciba Geigy AG) and p-(a-cumyl)phenol were charged, after confirmation of dissolution

and the liquid temperature was maintained at 110°C, manganese naphthenate (available from Wako Pure Chemical Industries, Ltd.) was formulated in the mixture as a reaction promoter, and the mixture was reacted for about 4 hours to synthesize a phenol-modified cyanate ester oligomer solution which is compatibilized with a polyphenylene ether resin.

Then, the reaction solution was cooled, and when the liquid temperature reached to 80°C, methyl ethyl ketone, a biphenyl type epoxy resin (3,3',5,5'-tetramethylbiphenol diglycidyl ether) (YX-4000) and a brominated bisphenol A type epoxy resin (ESB400T) were formulated in the mixture under stirring. Then, after confirmation of dissolution and the mixture was cooled to room temperature, p-tert-octylphenol (available from Wako Pure Chemical Industries, Ltd.) and zinc naphthenate (available from Wako Pure Chemical Industries, Ltd.) as a curing accelerator were formulated in the mixture to prepare a resin varnish having a non-volatile concentration of about 55% by weight.

#### EX-19

A resin varnish having a non-volatile concentration of about 55 % by weight was prepared in analogous to the procedure and formulation of EX-18 except that the brominated bisphenol A type epoxy resin (ESB400T) was removed from the above EX-18 formulation.

#### EX-20

A resin varnish having a non-volatile concentration of about 55 % by weight was prepared in analogous to the procedure and formulation of EX-18 except that the biphenyl type epoxy resin (YX-4000) was removed from the above EX-18 formulation.

#### (b) Prepreg

##### (Preparation of prepreg)

The resin varnishes obtained in EX-15 to 20 were each

impregnated into a glass cloth (E glass) with a thickness of 0.15 mm, and made through a gap of about 0.35mm. Then, the material was dried at 160°C for 4 to 7 minutes to obtain the respective prepregs with a resin solid content of 52% by weight.

(c) Copper clad laminated board

(Preparation of copper clad laminated board)

Four sheets of the above obtained prepregs were laminated, and copper foils with a thickness of each 18  $\mu$ m were provided on the both outermost layers, and molding was carried out under the pressing conditions of 230°C for 70 minutes and 2.5MPa by heating and pressure to prepare a both-surface copper clad laminated board.

(2) Evaluation method

(Evaluation methods of the characteristics of the copper clad laminated board)

With regard to the obtained copper clad laminated board, copper foil peeling strength, dielectric characteristics, solder heat resistance, water absorption rate, thermal expansion coefficient ( $\alpha$ ),  $T_g$  (glass transition temperature) and bending characteristics were evaluated. The evaluation results are shown in Table 2.

Evaluation methods of the characteristics of the copper clad laminated boards are as shown below.

Solder heat resistance of the copper clad laminated boards was examined by first etching the whole surface-copper foil (whole surface-copper foil etched product), and maintain in a pressure cooker tester (conditions: 121°C, 2.0 atm) for 2 hours, then, immersing in a molten solder at 288°C for 20 seconds, and the appearance thereof was judged with naked eyes. The number of test is  $n=3$ , in Table,  $\circ$  mean as no abnormality,  $\times$  mean as occurrence of measling or blister.

Thermal expansion coefficient ( $\alpha$ ) and  $T_g$  of the copper clad laminated boards (whole surface-copper foil etched

product) were measured by TMA(Thermal Mechanical Analysis).

Dielectric properties such as dielectric constant ( $\epsilon_r$ ) and dielectric dissipation factor ( $\tan \delta$ ) of the copper clad laminated boards were measured by a triplate structure line resonator method using a vector type network analyzer (IPC standard: IPC-TM650, 2.5.5.5.1). Incidentally, the measurement conditions are: frequency: 1 GHz, measurement temperatures: room temperature (25°C) and high temperature (90°C).

Water absorption rate of the copper clad laminated boards (whole surface-copper foil etched product) was calculated from a weight difference between the normal state and after maintaining in a pressure cooker tester (conditions: 121°C, 2 atm) for 5 hours (unit: % by weight).

Bending characteristics were obtained by measuring bending modulus at room temperature according to copper clad laminated boards test standard JIS-C-6481, breaking strength and breaking elongation at room temperature.

### (3) Results

The formulation and evaluation results are shown in the following Table 2.

Table 2: Formulation of Varnishes and property evaluation results of laminated board

Item	EX-15	EX-16	EX-17	EX-18	EX-19	EX-20
Cyanate compound						
Bisphenol A type cyanate ester(BADCY) (g)	300	300	300	-	-	-
Novolak type cyanate ester REX-371 (g)	-	-	-	450	450	450
Polypheylene ether resin (g)	-	-	-	225	225	225
Epoxy resin						
Biphenyl type Epoxy resin (YX-4000) (g)	-	120	57	160	160	-
Brominated Bisphenol A type Epoxy resin (ESB-400T) (g)	120	-	-	230	-	230
Phenol compound						
At reaction of oligomers: p-cumyl phenol (POP) (g)	36	36	36	13	13	13
At formulation of varnish: p-cumyl phenol (POP) (g)	-	-	-	-	-	-
At formulation of varnish: p-tert-octylphenol (POP) (g)	-	-	-	45	45	45
At reaction of oligomers: Zinc naphthenate (g)	0.200	0.200	0.200	-	-	-
Reaction Promoter						
At reaction of oligomers: Manganese naphthenate (g)	-	-	-	0.150	0.150	0.150
At formulation of varnish: Zinc naphthenate (g)	0.400	0.400	0.400	0.100	0.100	0.100
Solvent						
Toluene (g)	144	144	144	290	290	290
Methyl Ethyl Ketone (g)	102	102	68	630	440	498
VarnishNV(%)	65.0	65.0	65.0	55.0	55.0	55.0
Properties of laminated board						
Copper foil peeling strength (kN/m, 18 $\mu$ m, Normal copper foil)	1.5	1.5	1.5	1.5	1.5	1.5
$\epsilon r$						
1GHz(25°C)	3.85	3.55	3.52	3.58	3.53	3.62
1GHz(90°C)	3.75	3.57	3.53	3.59	3.54	3.71
$\tan \delta$						
1GHz(25°C)	0.0065	0.0055	0.0053	0.0054	0.0052	0.0058
1GHz(90°C)	0.0087	0.0058	0.0057	0.0059	0.0055	0.0079
Solder heat resistance (288°C)						
PCT-1h	000	000	000	000	000	000
PCT-2h	000	000	000	000	000	000
PCT-3h	00x	000	000	000	000	00x
PCT-4h	00x	000	000	00x	000	00x
PCT-5h	00x	00x	00x	00x	00x	00x
Water absorption rate(%)	0.56	0.51	0.50	0.54	0.52	0.53
TMA						
$\alpha 1$ (ppm/°C)	56	52	53	55	51	56
$\alpha 2$ (ppm/°C)	350	278	281	288	293	353
Tg(°C)	185	188	187	186	191	186
Bending properties (Room temperature)						
Bending modulus(GPa)	18	18	18	19	18	18
Breaking strength (MPa)	489	595	582	585	593	475
Breaking elongation (%)	3.1	3.7	3.7	3.6	3.7	3.0



EX-16 and EX-17, which are formulated with the biphenyl type epoxy resin (YX-4000) instead of brominated bisphenol A type epoxy resin (ESB400T) of EX-15, have good initial value of dielectric characteristics (dielectric constant  $D_k$  ( $\epsilon_r$ ) and dielectric dissipation factor  $D_f$  ( $\tan\delta$ )) and the difference (variable ratio) between the initial (room temperature) and high temperature (90°C) are smaller than EX-15, i.e. stable dielectric characteristics relative to temperature.

In addition, laminated boards of EX-16 and EX-17 are confirmed to show better characteristics in bending properties such as breaking strength and breaking elongation at room temperature (25°C).

Further, the laminated board of EX-18 replicated practically all characteristics of example 16 of the present application. Here, the effects of the present invention are maintained as EX-19, where the brominated bisphenol A epoxy resin (ESB-400T) is removed from the formulation of EX-18 making it solely of the biphenyl type epoxy resin (YX-4000) systems, showed slightly better results than that of EX-18 in dielectric properties, drifting property of dielectric characteristics and bending properties. On the other hand, EX-20, where biphenyl type epoxy resin (YX-4000) is removed from the formulation of EX-18 making it solely of the brominated bisphenol A epoxy resin (ESB-400T) systems, was confirmed to show much inferior results in the above properties.

#### (4) Consideration

In conclusion, the systems formulated with the biphenyl type epoxy resin showed the present effects (dielectric characteristics and stability of dielectric characteristics relative to temperature as well as mechanical properties (bending properties)) in the both formulation systems, one based on the prior art (Mizuno et al., example 19) and the other based on the present invention (example 16).

### III. Conclusion

I believe that the above results show that the unexpectedly better results achieved by the presently claimed invention in effects in direct comparison of presently claimed biphenyl epoxy resin composition with the brominated bisphenol A epoxy resin ESB-400T formulation disclosed in the closest prior art (Mizuno et al.).

IV. I further declare that all statements made herein of my own knowledge are true and that all statements made in information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: 2010, Jan., 12

Yasuyuki Mizuno  
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